SCIENCE AND TECHNOLOGY FOR ENERGY AND NATIONAL SECURITY

Celebrating 25 Years 1979-2004

CRF NEWS

COMBUSTION RESEARCH FACILITY

July/August 2005 • VOL. 27, NO. 4

Visiting researchers: CRF has far-reaching impact on combustion science and technology, careers

This article by CRF News editor Julie Hall continues a series commemorating the CRF's 25th anniversary.

When the CRF opened its doors to visiting scientists in 1980, Sandia managers weren't sure what to expect. Would the demand be there? What would be the response from the combustion community?

They didn't have to wait for long; inquiries from potential users were almost immediate. Twenty-five years and thousands of visitors later, the CRF is now considered to be a model user facility by the Department of Energy (DOE).

But numbers don't tell the whole story. Perhaps a more important metric—although difficult to quantify—is the CRF's impact on the science base, the engine industry, and researchers' careers. In the following vignettes, we look at three examples.

Axel zur Loye

Axel zur Loye came to the CRF in 1987 to work on a project funded jointly by Cummins Engine Co. and DOE. He had just received his Ph.D. from Princeton and been hired by Cummins, but instead of reporting to their Columbus, Ind., facility, he moved with his wife and son to Livermore for the nearly three-year project. He worked with CRF engineer Dennis Siebers to install a production-like Cummins engine in a lab and develop new two-dimensional imaging techniques to gain insight into particulate formation and oxidation processes.

(Continued on page 2)

Sandia National Laboratories

CRF scientists discover new combustion intermediates in hydrocarbon flames

The development of predictive models for combustion systems relies on detailed chemical mechanisms of hydrocarbon oxidation, which in turn rely on measurements in flames. While comprehensive chemical mechanisms have been developed for many fuels over the past 150 years, new work by an international team including CRF scientists demonstrates that an entire class of molecules missing from current oxidation models—the enols—occurs in a wide range of hydrocarbon flames.

The finding, published in the June 24 issue of *Science* (see www.ca.sandia.gov/crf/research/combustionChemistry/flameMeas/MBMS.php for links), will likely have a significant impact on prevailing hydrocarbon oxidation mechanisms, which are used in many areas of science, from understanding and reducing pollutant formation in combustion to describing partial oxidation in fuel cells. The finding is the most dramatic result so far from the flame machine developed at the Advanced Light Source at Lawrence Berkeley National Laboratory by researchers from the CRF, Cornell University, and the University of Massachusetts (see CRF News, July/August 2002). The team that discovered the enols included CRF researchers Craig Taatjes, Nils Hansen, Andrew McIlroy, Jim Miller, Stephen Klippenstein, and Juan Senosiain, and scientists from Cornell, the University of Massachusetts, the University of Bielefeld (Germany), and the National Synchroton Research Laboratory in Hefei, China., where a second synchrotron-probed flame machine is in operation.

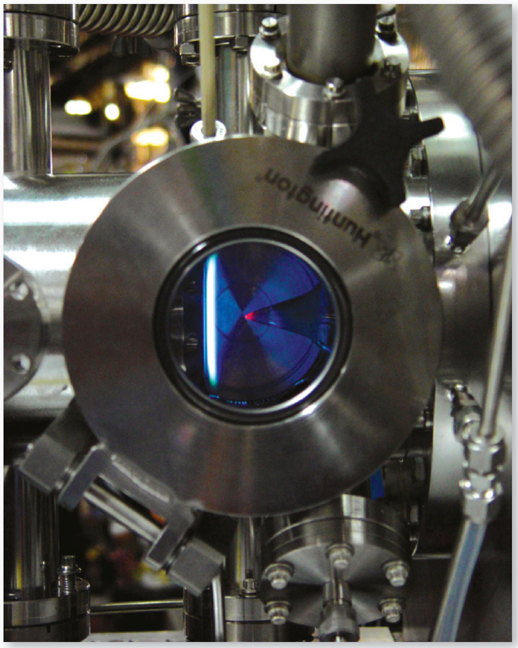


Figure 1. Flame apparatus at the Advanced Light Source. The flame is the glowing blue line; gases are sampled through a quartz cone (tip is glowing red), ionized by the ALS beam, and mass spectrometrically analyzed.

Elusive enols

Enols are the less-stable isomers of other well-known combustion intermediates such as aldehydes and ketones. Despite more than 150 years of flame chemistry investigation, dating back to the work of pioneers like Bunsen and Faraday, this entire class of molecules has remained undetected. While Erlenmeyer in 1880 predicted their existence as transient chemical intermediates, the simplest enol, vinyl alcohol, was not directly observed until 1973.

Because of their instability, enols have not been included in detailed combustion chemistry models. However, the new results show substantial concentrations of 2-, 3-, and 4-carbon enols in low-pressure flames of many elementary fuels and in flames of commercial gasoline. Hydrocarbon oxidation mechanisms must be modified to account for formation and removal of these unexpected compounds.

(Continued on page 6)

Visiting researchers *(Continued from page 1)*

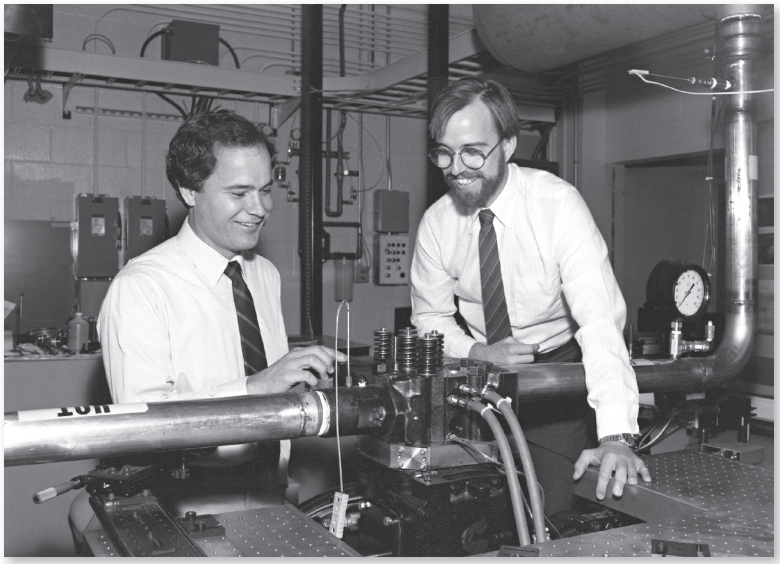
"What was new was the engine was very close and faithful to a production engine," said zur Loye, now director of advanced product development of natural gas engines at Cummins. "Before that the optically accessible engines were not based on real engines and in many ways did not look like real engines. The combustion part and the fuel injection system were very close to a production system, which was extremely important to Cummins."

The work forged a solid relationship between Cummins and Sandia that continues to this day, zur Loye said. It made important contributions to the understanding of diesel combustion and pollutant formation and also led to follow-on work (see below) that culminated in the development of a new description of diesel combustion.

"(All of this) work helped us develop the new engine technology to be able to very successfully meet increasingly challenging emissions regulations," zur Loye said.

Back then, few places were capable of doing this type of research, he said. And there's still a strong need today. To do this more fundamental work, you need a critical mass of experts in various fields who can interact with each other and feed off each other's ideas, and who have access to state-of-the-art equipment. Research done by Cummins and the engine industry is by necessity product-focused. The CRF pushes the state-the-art in terms of knowledge and understanding.

"A key place where that understanding comes into play is in modeling tools that are used by the industry," he said.



This 1988 photo shows Dennis Siebers (left) and Axel zur Loye of Cummins working on an optically accessible diesel research engine. The two collaborated for nearly three years.

Christoph Espey

About a year after zur Loye left the CRF, Chris Espey arrived. Cummins sponsored Espey, who had just completed his master's degree at Penn State University, to do his Ph.D. work at the CRF studying fuel-air mixing in the diesel process.

Working with Sandians John Dec and Eldon Porter, Espey built a new research engine. He outfitted it with quartz windows to allow full optical access into the combustion chamber. The engine, which is still in use at the CRF today, became the gold standard at the time for optical access engines. Cummins later used the design to build their own research engine.

Espey used the engine to develop an understanding of the liquid-phase fuel distribution in the diesel spray and to make quantitative two-dimensional measurements of the vapor-fuel/air ratio in the engine. Dec's investigations focused on soot distributions "so we developed a good understanding of the entire process from fuel injection, mixing, to the first formation of pollutants," Espey said.

The team mapped out the way fuel mixes with the in-cylinder air and where soot formation occurs, permanently changing the picture of diesel engine combustion. This new conceptual model showed engine designers where to best focus their efforts toward minimizing emissions to reach solutions faster and at lower cost. Previously, model developers knew little more than how fast the fuel burned and what emissions came out the tailpipe. The more than four-year collaboration resulted in eight publications.

After getting his Ph.D. from Penn State in 1994, Espey was offered a job by Daimler (now DaimlerChrysler), where he is now in charge of aftertreatment and fuel-injection systems for truck engines. He has built five research engines for the company modeled after the engine he helped build at the CRF. While he returned to the CRF briefly in 1996 to do additional research, Espey calls his four-year stint there a "one-time opportunity." While he could have done his Ph.D. in Germany, he wanted to apply laser diagnostics to the study of fundamentals of diesel combustion.

"I don't think I would have been able to do that type of research and obtain those kind of results anywhere else," he said.

Volker Sick

Volker Sick has been a frequent visitor at the CRF for more than 10 years—a tradition he is also passing along to his students. As a mechanical engineering professor at the University of Michigan, Sick has had three graduate students work at the CRF with funding from the National Science Foundation, the DOE, and the CRF. They have worked closely with CRF staff researchers on investigations of picosecond laser-induced fluorescence of nitric oxide in flames, turbulence in diesel engines, and emissions measurements in a homogeneous-charge compression-ignition engine.

"The CRF provides an excellent place for research that requires unusual, unique equipment and expertise," Sick said.

This combination of equipment and outstanding researchers is what first drew him to the CRF in 1993, shortly after completing his doctorate at the University of Heidelberg. He was familiar with the CRF's work, and a colleague from the University of Heidelberg had spent two years there. With Roger Farrow as his host, he spent two months at the CRF working on degenerate four-wave mixing techniques. Based on what he achieved during that visit, he received funding from the German Science Foundation for a one-year research fellowship starting in July 1994 on projects related to four-wave mixing.

Over the next 10 years, Sick has returned to the CRF numerous times for visits ranging from a few days to about a month.

"The CRF brings together researchers from all over the world and provides an outstanding networking opportunity," he said. "I have seen many long-term collaborations and friendships started this way."

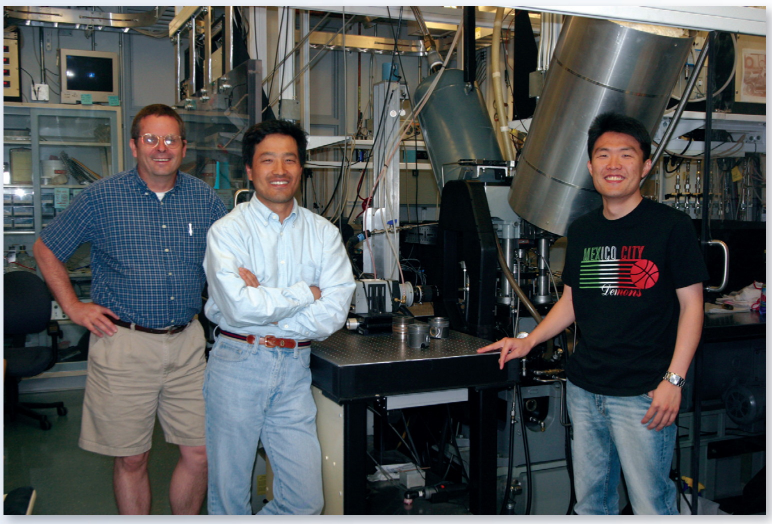
Dawn Manley

CRF appoints new manager

Dawn Manley has been promoted to lead the CRF's Reacting Flow Research Department, where she will oversee experimental and computational modeling studies of reacting flow phenomena relevant to combustion processes. She replaces Andy McIlroy, who assumed the Combustion Chemistry Department manager position upon the departure of Sarah Allendorf, who took another management position at Sandia.

Manley had worked in the Systems Studies Department since joining Sandia in 1999. Her most recent project was to lead the systems modeling and analysis effort under BioNet, a joint program between the Department of Homeland Security and the Defense Threat Reduction Agency that seeks to manage the consequences of a biological attack. BioNet involves Sandia, Los Alamos, and Lawrence Livermore national laboratories, as well as a several other public and private institutions. Manley has a bachelor's degree in chemical engineering from Stanford University and a Ph.D. from Princeton University.

Postdoc Dae Choi (center) left the CRF in May to return to Korea. He had worked with CRF engineer Paul Miles (left) for three years on low-emission combustion systems for automotive diesel engines. Also pictured is Sanghoon Kook, a visiting Ph.D. student from Korea.



A new Web site devoted to the Department of Energy's Metal Hydride Center of Excellence (MHCoE) has been launched at www.ca.sandia.gov/MHCoE. The site describes the work of the 17 research partners in the center, which is a government-industry-university research effort focused on developing a safe, economical hydrogen storage system based on reversible metal hydrides for use in vehicles.

Established in 2004 by the U.S. Department of Energy, the MHCoE is led by Sandia National Laboratories and is one of three Centers of Excellence established in support of President Bush's Hydrogen FreedomCAR and Fuel Initiative.

Mueller receives speaker award

CRF engineer Chuck Mueller is among the eight recipients of the 2005 Lloyd L. Withrow Distinguished Speaker Award from the Society of Automotive Engineers (SAE). The award recognizes individuals who have received SAE's Oral Presentation Award more than twice. It honors the late Lloyd L. Withrow, former head of General Motors Research Laboratories Fuels and Lubricants Department, and a noted speaker at many SAE meetings.

Mueller has been a staff member in the Engine Combustion Department since 1996, performing research in the areas of optical combustion diagnostics and fuel effects on advanced compression-ignition combustion processes.

CRF manager Andy McIlroy (left) visits with former Sandian Steve Vosen and former CRF manager Sarah Allendorf. Vosen is a Bay Area patent agent.

CRF to host 25th anniversary technical symposium

The CRF will host a technical symposium, "Energy and the Future of Energy R&D" on Nov. 17, 2005, at Sandia National Laboratories in Livermore, Calif. The event will feature the following speakers, who will discuss opportunities and challenges faced by the scientific community in preparing for future energy demands.

Speakers:

Marilyn A. Brown
Director, Energy Efficiency, Reliability, and Security
Oak Ridge National Laboratory
Member, National Commission on Energy Policy

Alan C. Lloyd
Secretary, California Environmental Protection Agency
Chairman, California Air Resources Board

Margo T. Oge
Director, Office of Transportation and Air Quality
U.S. Environmental Protection Agency

Paul Roberts
Journalist and Author
Author, *The End of Oil: On the Edge of a Perilous New World* and frequent contributor to *Harper's* magazine

*Further details on the symposium will be posted at **www.ca.sandia.gov/crf** as they become available.*

Celebrating 25 years at the Combustion Research Facility

Current and former staffers commemorate the founding of Sandia's first user facility

Returning "alums" joined with current staff members and managers on May 20 for a "reunion" in celebration of the Combustion Research Facility's (CRF) 25th anniversary. The celebration drew about 150 attendees for an informal afternoon ceremony that included remarks by current and former CRF directors, a reunion video, and visits to labs.

CRF Deputy Director Bob Carling, who emceed the event, has been with the CRF since 1986.

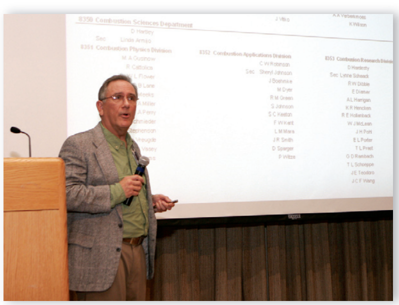
Deputy director Bob Carling, who emceed the event, made a special presentation recognizing five current staff members and managers who have been at the CRF since its beginning as "CRF originals." The individuals are Don Hardesty, Pete Witze, Jim Miller, Larry Rahn, and Alan Kerstein.

Founding director Dan Hartley, who was out of the country and unable to attend, sent videotaped remarks in which he touched on important people, events, and milestones in the establishment of the CRF. He recalled the energy crisis of the early 1970s in which Americans experienced long lines at gas stations and gasoline rationing. "We had a passion to do something about those gas lines," he said.

He recalled the "unexpected gift" that Sandia received from Volkswagen during his two-year benchmarking tour of facilities in Europe that were conducting combustion research. Volkswagen offered Sandia a combustion simulator with optical access that had taken years to develop. Sandia researchers were able to quickly get it operational. "That was a remarkable gift that got us going at a very important time," Hartley said.

(From left) Larry Rahn, Jim Miller, Don Hardesty, and Pete Witze have all worked at the CRF since it opened in 1980. They were recognized during the reunion ceremony as CRF "originals." Not pictured is Alan Kerstein.

Former directors Peter Mattern and Bill McLean also spoke, as did current director Terry Michalske. Former Sandia/CA Vice President Tom Cook joined the gathering by phone.



Former CRF director Peter Mattern uses a 1980s CRF organizational chart to point out attendees in the audience.

Researchers seek to improve bioterrorism agent early-warning sensors

Increased attention to bioterrorism defense since the 2001 anthrax attacks has led to the deployment of a variety of developmental early-warning sensors to detect potential bioaerosol agents in U.S. public facilities. However, the sensors, which typically employ laser-induced fluorescence (LIF) to infer the presence of amino acids and other biomarkers, produce false alarms at an unacceptable rate.

With funding from the Department of Homeland Security (DHS), CRF researchers Tom Kulp and Scott Bisson are collaborating with researchers at Yale University (Yong-Le Pan and Richard Chang) and the Army Research Laboratory (Ron Pinnick) to better understand the chemical and physical properties of ambient particulates that can confound existing biosensors. Their selective particle detector has generated information regarding background particulates that will be used to address ways of improving early-warning sensors. This work is being done concurrently with a year-long field evaluation of existing sensor performance by Sandians Tom Reichardt (another CRF researcher), Renata McCoy, and Kevin Schroder.

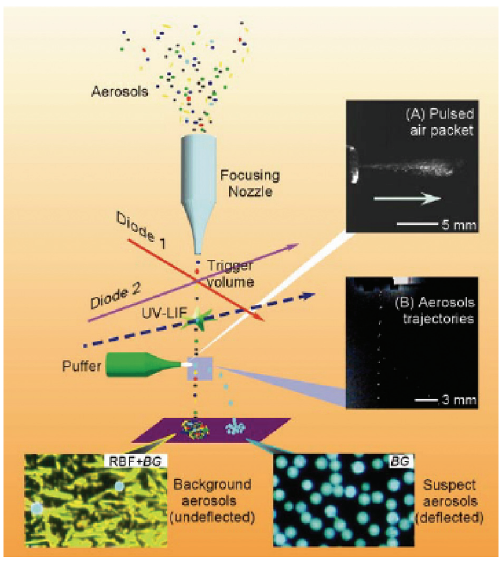


Figure 1. Diagram depicting the operation of the selective particle collector. Aerosols are concentrated from the air and formed into a stream using a focusing nozzle. Scattering from a crossed pair of diode lasers indicates the presence of a particle. If present, the particles are excited to fluoresce by a UV laser. If the fluorescence spectrum meets a predefined condition, the supersonic valve ("puffer") is activated to deflect the particles to a collection region. The lower images indicate successful separation of a mixture of riboflavin crystals from BG (*Bacillus globigii*) spores using this method.

Addressing sensor limitations

Early-warning sensors for bioaerosol agents must rapidly (~1 minute) indicate the presence of an agent release and, potentially, trigger species identification by higher-resolution (but slower) instruments. While the speed and sensitivity of LIF make it the technology of choice for warning/trigger devices, the relatively nonspecific nature of biological emission spectra leads to a high false-alarm rate.

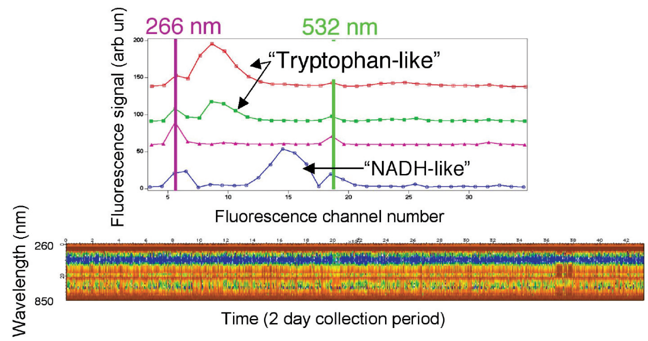


Figure 2. Spectra taken with the system during a two-day portion of the deployment at the airport. The graph (top) shows individual single-particle fluorescence data, indicating spectra that show emission in the regions where tryptophan and nicotinamide adenine dinucleotide (NADH) emit. The lower image shows a compilation of 43,277 "tryptophan-like" spectra collected during the sampling period. Colors indicate fluorescence intensity with brown being weakest and blue most intense.

The Sandia study addresses this problem using a Yale/ARL-developed instrument at a sensor testbed operated by Sandia at a major international airport. The system serves as both a fluorescence spectrometer and a selective aerosol collector.

As shown in Figure 1, particles from the air are concentrated into a flowstream within the device where their fluorescence spectrum is measured. If particles are present (indicated by scattering from a crossed pair of diode lasers), they are excited to fluoresce using an ultraviolet laser. The magnitudes of optical signals in the 32 spectral emission channels and the elastic scattering (at the laser wavelength) channel are input to an algorithm that decides whether a particle should be retained for further analysis. This algorithm can be set up to mimic the algorithm used in a commercial biosensor (currently limited to 2 or 3 emission channels), thus identifying particles that would lead to a false alarm in such a device. If a particle is to be retained, a puff of air from a supersonic nozzle deflects these particles toward a surface where they adhere.

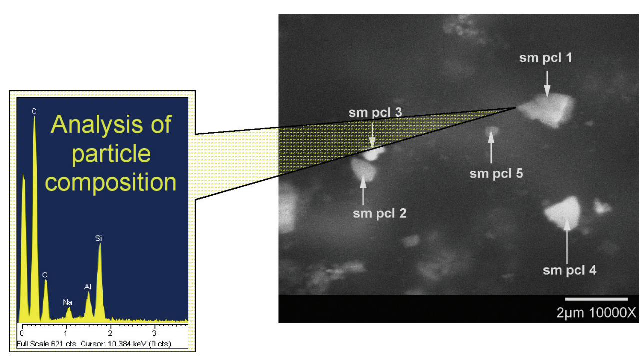


Figure 3. Scanning electron micrograph (right) of particles collected at the airport that exhibit tryptophan-like fluorescence. Also shown is an energy-dispersive X-ray analysis (EDXA) spectrum of one of those particles (left).

(Continued on page 6)

Enols (Continued from page 1)

Technology enabled discovery

The discovery of enols was made possible by the powerful combination of molecular beam mass spectrometry (MBMS) with photoionization by tunable vacuum ultraviolet (VUV) synchrotron radiation (see Figure 1). Gases are sampled from a low-pressure premixed laminar flame, ionized by the VUV light, and analyzed by time-of-flight mass spectrometry. The strength of this combination lies in the ability to distinguish isomers based on their photoionization energy. Enols can be ionized by less energetic photons than their keto (aldehyde or ketone) counterparts. Therefore, the contribution of enols can be readily isolated.

Enols were present in concentrations 10–100 times what would be expected by simple keto-enol isomerization, indicating separate formation mechanisms for the isomers. Figure 2, taken from the *Science* article, shows photoionization efficiency spectra for m/z = 44 ions (the mass of ethanol or acetaldehyde) sampled from four of the 24 flames investigated, along with the fraction of the m/z = 44 signal attributable to ethenol. Furthermore, the concentration profiles of the enols as a function of position in the flame demonstrates that their removal cannot be dominated by tautomerization to the keto form. Enols should react rather differently from aldehyde or ketone isomers, but very little is yet known about gas-phase neutral enol reactions. Therefore, the consequences of this discovery remain uncertain. Explaining how enols form and what their fate is in combustion will require considerably more experimental and theoretical study.

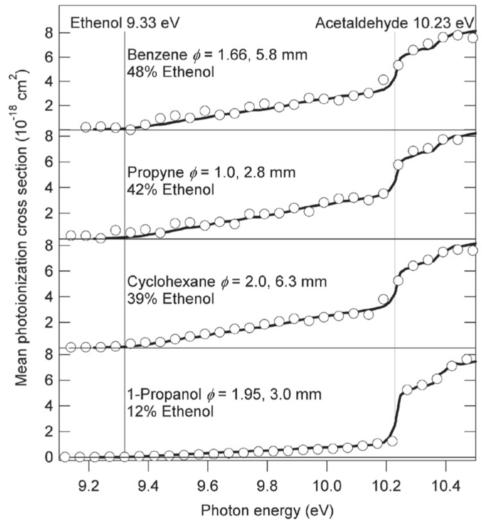


Figure 2. Fractions of enols in several flames, as revealed by photoionization mass spectrometry. Ionization energies for acetaldehyde (CH_3CHO) and ethenol (vinyl alcohol, CH_2CHOH) are shown as the vertical lines. The fraction of C_2H_4O signal attributable to ethenol is given for each flame. The equivalence ratio φ (ratio of fuel to oxygen relative to a stoichiometric mixture) and the distance from the burner are also given.

Sensors (Continued from page 5)

Evaluating potential improvements

Both the collected particles and their fluorescence spectra are analyzed to yield critical information regarding the properties of interfering particles in an airport environment. To date, the instrument has collected several million single-particle fluorescence spectra (see Figure 2), allowing the researchers to analyze the spectral shape of the emission and to assess the utility of adding more emission channels to existing instruments. More importantly, as shown in Figure 3, analysis of the collected particles has revealed information regarding their chemical composition and physical properties that can be used to explore alternate means of suppressing false alarms in UV-LIF sensors or to suggest new sensing mechanisms. These collected particles are also available as sample sets to test alternate screening methods. The researchers will be developing and testing these more advanced methods during a second phase of the program, to be conducted in the coming year.

Sandia National Laboratories

Mail Stop 9052
P.O. Box 969
Livermore, California 94551-0969

TEMP - RETURN SERVICE REQUESTED

PRESORTED
FIRST CLASS
U.S. POSTAGE
PAID
SAN LEANDRO, CA
PERMIT # 311

CRF News is a bimonthly publication of the Combustion Research Facility, Sandia National Laboratories, Livermore, California 94551 0969.
ISSN 1548-4300

Director .... Terry Michalske
Editor .... Julie Hall
Graphic Artist .... Daniel Strong
Photography .... Daniel Strong & various photographers

Subscriptions are free. Subscriptions and address changes to Julie Hall, jchall@sandia.gov.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC0494AL85000